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THE ADSORPTION OF AMMONIA BY
SILICA GEL.

Dissertation

Submitted to the Board of University Studies of the Johns
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the Degree of Doctor of Philosophy

by

Levi Yorgéy Davidheiser
"
Baltimore

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CONTENTS

Acknowledgment - - - - -	
Introduction - - - - -	1
Apparatus - - - - -	2
Material - - - - -	2
Procedure - - - - -	3
Tables - - - - -	6
Graphs - - - - -	12
Biography - - - - -	13

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THE ADSORPTION OF AMMONIA BY SILICA GEL

The following investigation is a continuation of our studies of adsorption of gases and vapors by silica gel. In Göttingen with Zsigmondy the adsorption of NH_3 , SO_2 and CO_2 of silica gel was studied. Since then many improvements in experimental technique have been introduced, as well as radical modifications of the theoretical treatment of the experimental results. The experimental method and an outline of our theoretical views have been given in a paper dealing with the adsorption of SO_2 .¹

The adsorption of ammonia was studied for a number of reasons. In the first place, this gas, in the measurements made in Göttingen, was found to be more strongly adsorbed than SO_2 although the latter exhibits a higher critical temperature. In the second place, our previous measurements indicated that the behavior of ammonia was analogous from the standpoint of the rate at which equilibrium was reached. Again, ammonia is extremely soluble in water and it was therefore hoped that by a careful study of its adsorption by silica gel, light would be thrown on the question as to the nature of the small amount of water that is always associated with the gel. Furthermore, in ammonia we have a gas that has been the subject of numerous careful investigations, and as a result the physical constants, such as vapor pressure, density and surface tension, are very accurately known. This latter point is especially important inasmuch as a knowledge of the above constants is necessary for the testing of our theoretical views as to the course of the adsorption.

¹ MacGavack & Patrick, J.A.C.S. 42, 946 (1920)

In the following measurements of the adsorption of ammonia by silica gel, it will be shown that the behavior of this gas is not analogous to former measurements, either from the standpoint of the extent or the rate of the adsorption, the earlier discrepancies being due to the uncertain water and acid content of the gel. Especial study was made of the influence of the water content of the gel on the adsorption, it being found that small differences of the same produced large variations in the adsorptive ability of the material.

APPARATUS

The experimental method has been described in detail by MacGavack and Patrick.¹ To give an idea of the precision attained, it may be stated that the volume of ammonia was measured to within 0.005 cc., the pressure to within 0.03 mm., and the temperature of the thermostat regulated so as not to vary more than 0.05°.

MATERIAL

The ammonia used was purified liquid ammonia. Commercial ammonia was treated with metallic sodium for one week, allowing the accumulated gas to escape at intervals of twelve hours. The purified sample was tested by allowing a small stream of the gas to bubble into sulphuric acid contained in a gas burette for ten minutes; as no residue was shown by this procedure it was assumed that the ammonia was free from permanent gases.

The silica gel was an ordinary commercial sample that was further purified by treatment with nitric acid and a thorough washing with distilled water. When dried in a vacuum of 1 - 5 mm. at a temperature of 300° for three hours the gel still contained 5.21% of water, and furthermore, an appreciable amount of nitric acid, to which reference will be made later.

¹loc. cit.

PROCEDURE

The adsorption apparatus was evacuated by means of a rotary oil pump and a Gaede mercury pump, connected in series. Before any gel was put into the adsorption bulb, the apparatus was thoroughly evacuated and then swept out with ammonia and evacuated again until the MacLeod gage showed no pressure after standing under a vacuum for forty-eight hours. The gel was weighed in the adsorption bulb, which was then directly attached to the apparatus by means of a ground joint, and mercury sealed. The pumps were always started before the stop cock between the adsorption bulb and the main apparatus was opened, so that the air in the bulb would have less chance to become adsorbed on the walls of the apparatus. The heating of the adsorption bulb was started at the same time, care being taken not to heat the gel to a higher temperature than that at which it was prepared, so that the water content might not be disturbed. The evacuation was continued until the MacLeod gage showed no pressure, usually from three to eight hours, at a temperature from 290° to 300° .

In the beginning it was found almost impossible to make two determinations that would agree. After a considerable number of measurements were made at 30° , a few were found to check fairly well. However, a number of measurements made at 40° showed that the gel exhibited greater adsorptive ability at this temperature than at 30° . Such inconsistent and disturbing results lead us to stop and thoroughly inspect our apparatus and method of procedure. The apparatus was first examined for leaks. It was thoroughly evacuated and allowed to stand for one week, at the end of which the MacLeod gage showed no increase of pressure. The ammonia was again examined and no foreign gases found.

Another series of measurements were made at 30° in which great care was taken that all manipulations should be as nearly identical as possible. The electric furnace, in which the adsorption bulb was heated during evacuation, was kept constant and evacuation continued for exactly the same length of time. Under these conditions checks could be made with but little variations. This proved that the gel did not remain constant during evacuation, especially was this true when the pumps were run different lengths of time. All the experiments recorded in this paper were made under conditions that allow for exact duplication.

In tables XX, XXIII, XXV and XXIX are recorded the results of the measurements made at 0° , 30° , 40° and 100° . These results are shown graphically in Fig.I. Equilibrium was usually reached in from fifteen to thirty minutes, nevertheless the ammonia was allowed to remain in contact with the gel at least two hours. As more ammonia was introduced and the pressure increased, the time required to reach equilibrium also increased. If equilibrium was not reached within two hours after the introduction of the first amount of ammonia, it served as a criterion that the air had not been completely removed from the apparatus. It was found that three hours evacuation with the adsorption bulb heated to 290° was sufficient to remove all the air. All the determinations were made under these conditions. After this treatment it was found that the gel lost 0.28% of its water content. If this treatment was continued for eight hours 0.487% of the water was removed. The gel upon analysis was found to contain 0.437% nitric acid, equivalent to 5.23 cc. of ammonia. Of course as the gel lost some of its water content some of the acid was also lost.

Inasmuch as our preliminary measurements showed that the water content of the gel was a most important factor in determining

the extent of the adsorption, an effort was made to prepare a low water content gel. It has been previously thought that the presence of the water was very closely associated with the structure of the material and the removal of the water below 2% was considered undesirable. The subsequent results, however, indicate that such views are unsound and that it is possible to obtain a gel possessing the proper adsorptive structure having only 0.33% water.

A gel containing 0.33% water was prepared by heating it in a pyrex glass tube through which a current of dry air was passed. The tube was gradually heated with a Bunsen flame for one hour, and then in the flame of the blast lamp for two hours to the fusion point of pyrex glass. During this process the gel became perfectly clear and colorless.

After this treatment the gel was tested for its ability to adsorb ammonia. It was rather surprising to find that it was still a good adsorbent for ammonia, adsorbing on an average about 53 cc. less per gram than it did before this drastic treatment. Two isotherms were made, one at 0° and one at 30°. Fig. III shows the graph of these determinations as compared with those made before dehydrating the gel. Tables XXXI and XXXV show the experimental results.

It is necessary to mention a phenomenon that was observed with the measurements made at 100°. After 33.64 cc. of ammonia had been brought over 0.5741 grams of gel and the pressure had reached a value of 287.35 mm., it was noticed that there was a gradual increase in the pressure. This increase in pressure continued until at the end of nine days the pressure in the apparatus was 471.40 mm. Upon cooling the gel to 0°, the pressure immediately dropped to 4.53 mm., while heating again to 100° caused an immediate rise in pressure to the value of 471.40 mm. That this phenomenon is in some way associated with the water of the gel is indicated by the fact that no such behavior as outlined above was exhibited with the gel containing only 0.33% water.

P = equilibrium pressure in cm. of mercury.

X/M = cc. of ammonia under standard conditions
adsorbed per gram of gel.

V = cc. of liquid ammonia adsorbed.

Po = vapor pressure of liquid ammonia.

D = density of liquid ammonia.

= surface tension of liquid ammonia.

EXPERIMENT XXIX

Temp. 100° H₂O content 4.93% Wt. of gel 0.5737 gr. D 0.4589 σ 6.5

$\frac{1}{M}$.2885 K 23.07 Po 4693.40

P	X/M	V	$\frac{P\sigma}{Po}$
2.147	27.05	.04473	.00276
13.805	52.22	.08636	.01912
41.016	66.62	.11017	.05681

EXPERIMENT XXIII

Temp. 40° H₂O content 4.93% Wt. of gel 0.5730 gr. D 0.5769 σ 16.70

$\frac{1}{M}$.2093 K 53.53 Po 1165.80

P	X/M	V	$\frac{P\sigma}{Po}$
0.218	36.42	.050	.003123
4.026	77.03	.101	.057672
20.987	101.06	.133	.300622
61.632	126.25	.166	.882887

EXPERIMENT XX

Temp. 30° H₂O content 4.93% Wt. of gel 0.5739 gr. D 0.5939 σ 18.03

$\frac{1}{M}$.2103 K 57.30 Po 874.90

P	X/M	V	$\frac{P\sigma}{Po}$
.07	26.82	.034	.001443
1.009	68.05	.087	.020792
37.726	126.66	.161	.683757

EXPERIMENT XXV

Temp. 0° H₂O content 4.93% Wt. of gel 0.5744 gr. D 0.6389 σ 25.94

Po 322.10 $\frac{1}{M}$.2116 K 82.40

P	X/M	V	$\frac{P\sigma}{Po}$
.153	58.77	.070	.012321
8.116	123.47	.147	.654614
33.494	168.59	.200	2.697404
58.653	191.99	.228	4.723902

EXPERIMENT XXXI

Temp. 30° H₂O content 0.33% Wt. of gel 0.5739 gr. D 0.5959 σ 18.03

$\frac{1}{M}$.2487 K 21.33 Po 874.90

P	X/M	V	$\frac{P\sigma}{Po}$
1.293	24.49	.03113	.026646
8.653	46.00	.05878	.178021
18.933	57.08	.07294	.390173
36.600	73.50	.09392	.754265
59.697	83.01	.10608	1.23024

EXPERIMENT XXXV

Temp. 0° H₂O content 0.33% Wt. of gel 0.5739 gr. D 0.6389 σ 25.94

$\frac{1}{M}$.3948 K 28.765 Po 322.10

P	X/M	V	$\frac{P\sigma}{Po}$
3.391	47.85	.05684	.273091
6.763	61.35	.07287	.544651
13.964	80.54	.09567	1.124572
46.066	127.50	.15145	3.708976
61.365	145.44	.17276	4.941874

DISCUSSION OF RESULTS

The various isotherms may be very accurately represented by the ordinary imperial adsorption formula, $\frac{x}{M} = K P^{\frac{1}{n}}$. In Fig.II are plotted the logarithms of x/M against P , and from the straightness of the lines it is apparent that the above formula accurately reflects the experimental data. Inasmuch as the SO_2 was also well represented by the same relationship, the comparison of the behavior of NH_3 and SO_2 is greatly facilitated by use of the values of K at the same temperature. In the following table are given the values of K for SO_2 and NH_3 obtained with a gel of approximately the same water content, 4.8%.

	NH_3	SO_2
	K	K
0°	82.40	29.14
30°	57.30	12.93
40°	53.53	9.75
100°	23.01	1.12

Inasmuch as the significance of K is the number of cc. of gas adsorbed by 1 gram of gel at a pressure of 1 cm., it is apparent that ammonia is more strongly adsorbed than sulphur dioxide by this particular sample of gel.

That this result is due to the larger solubility of ammonia in water, is shown by the fact that the value of K for NH_3 at 0° decreased from 82.40 to a value of 28.76 when the water content was reduced from 4.88% to 0.33%. While it is true that the adsorption of SO_2 is lessened by a diminuation of the water content of the gel, the effect here is not so pronounced as in the case of NH_3 . It will be observed that with a gel containing 0.33% water content, the adsorption of NH_3 is lower than that of SO_2 in a gel containing 4.87% water. It is our belief

that with an anhydrous gel the adsorption of NH_3 will be found to be in accordance with its ease of condensation as expressed by its critical temperature.

The above results for ammonia must also be corrected for the acid that is present in the gel. In the beginning it was thought that prolonged washing with distilled water was sufficient to remove all acid, especially inasmuch as the acid diffuses readily through the gel when in the state that it is when washed. Nevertheless, upon collecting the liquid that is driven off from a gel containing 5.21% water by heating to $800^\circ\text{--}900^\circ$, the same was found to require 0.653 cc. of 0.1066 N alkali for the neutralization per gram gel. This acid would probably not exert an appreciable effect upon an acidic gas such as SO_2 , but would materially affect the adsorption of NH_3 .

The above facts illustrate the great need for care when generalizations are drawn concerning adsorption. It is apparent that the amount of NH_3 that the gel is capable of taking up depends not only on the capillary structure of the gel, but in addition upon the water and acid content. Before generalizations as to the effect of capillarity on adsorption may be drawn, it is necessary to allow for the solubility of the gas in the water and the amount of NH_3 that combines with the acid present.

If instead of expressing the weight of NH_3 taken up by a unit weight of gel under a certain pressure, the volume of liquid ammonia adsorbed per gram of gel under condensation pressure is used, all the isotherms fall on a smooth curve which may be expressed by the equation $V = 0.671 \left(\frac{P_T}{P_0} \right)^{2.105}$. These results are shown in Fig. IV and Fig. V, where will be found plotted the logarithms of the volume of NH_3 adsorbed against the logarithms of the condensating pressures $\left(\frac{P_T}{P_0} \right)$.

A similar result was obtained with the SO_2 measurements where the values of K and $\frac{1}{M}$ were .1039 and .447 respectively. In the case of NH_3 with a gel of 4.88% water content, the equation becomes . While with a gel of 0.33% water content K has the value of .0955 and $\frac{1}{M}$.3588.

At first thought it may be considered strange that the above formula should apply to the adsorption of NH_3 when we consider the very large portion of the NH_3 that is dissolved in the water of the gel. This behavior is immediately explained, however, from the fact that the solubility of NH_3 in water may be expressed by the same formula as is used to express the results of the adsorption of NH_3 by silica gel. In other words, as shown by measurements made in this laboratory, the solubility of NH_3 in water is well represented by the formula,

It has also been shown that the solubility of sulphur dioxide in water may be well represented by the above formula where $K = .0123$ and $\frac{1}{M} = .91$. It is therefore possible to calculate the adsorption due to the capillary structure alone by correcting, with the aid of the above formula, for the amount of gas dissolved in the water of the gel. Applying this formula, $V = K \left(\frac{p}{p_0} \right)^{\frac{1}{4}} + 0.48 K' \left(\frac{p}{p_0} \right)^{\frac{1}{4}}$, to the measurements of NH_3 made with the gel containing 4.8% water, and taking the mean K becomes .1147. Doing the same with the measurements of SO_2 , we find that the mean for K does not differ much from .1038. The K for the anhydrous gel is .0955. From these experiments we see that the amount of different gases adsorbed due to capillarity is in good agreement.

Fig. I

x/M
cc. x 0.6

0

0

0

0

0°

30°

40°

100°

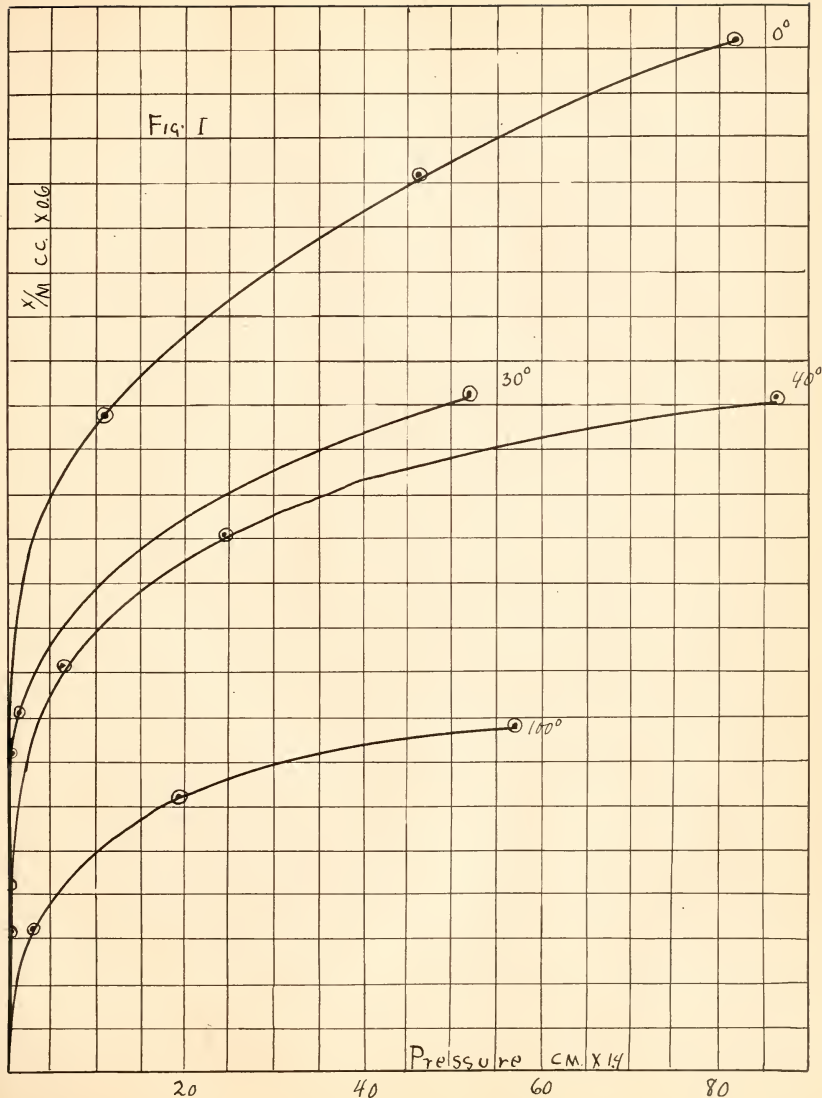
Pressure cm. x 14

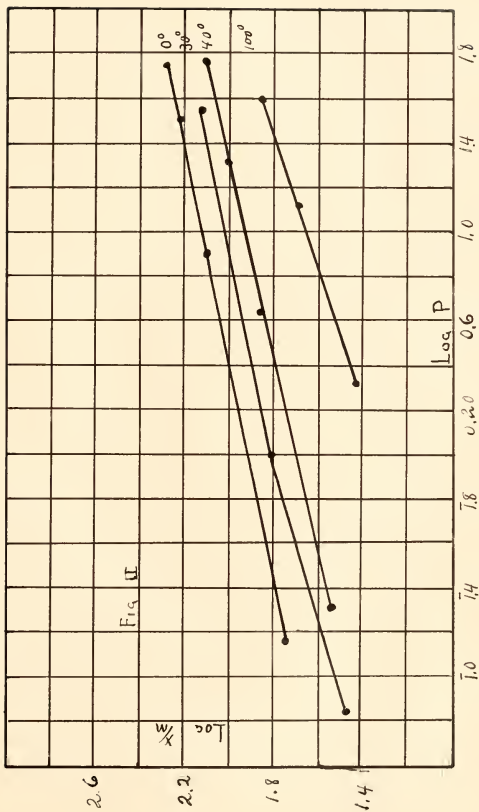
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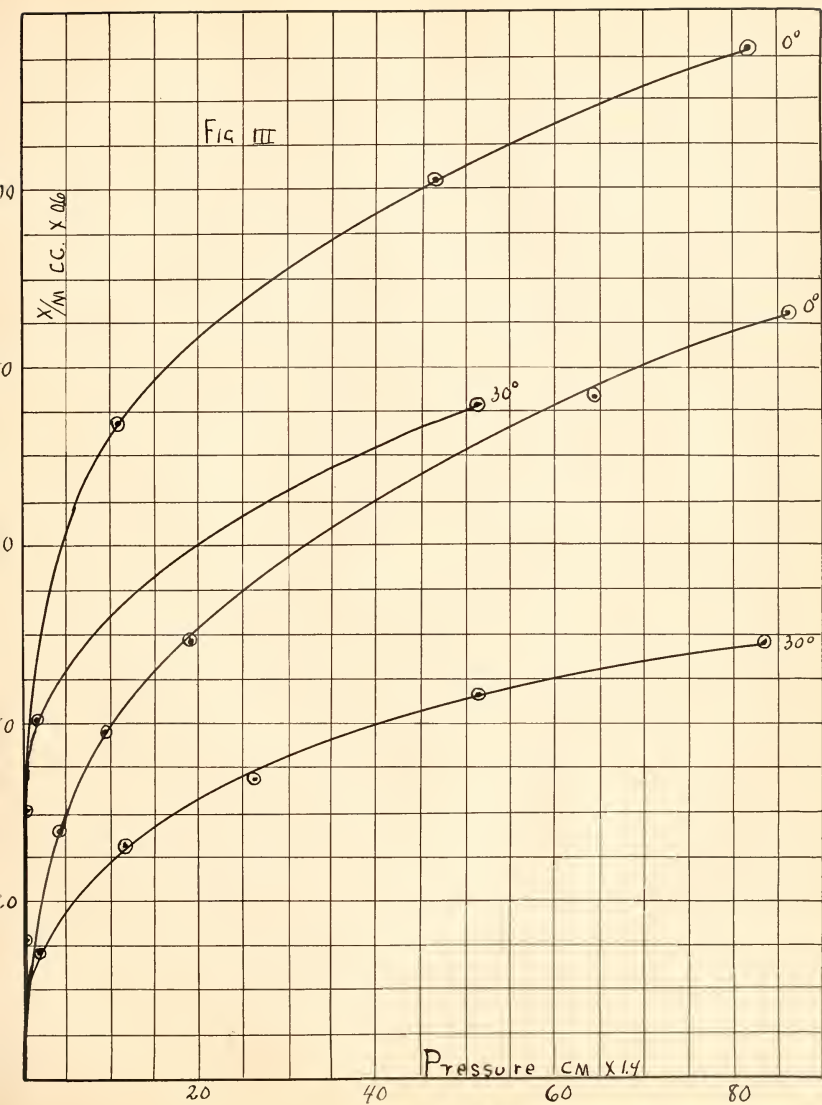
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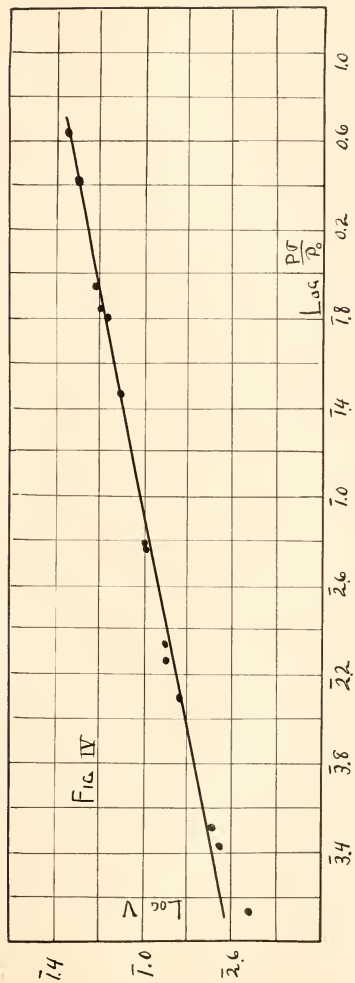
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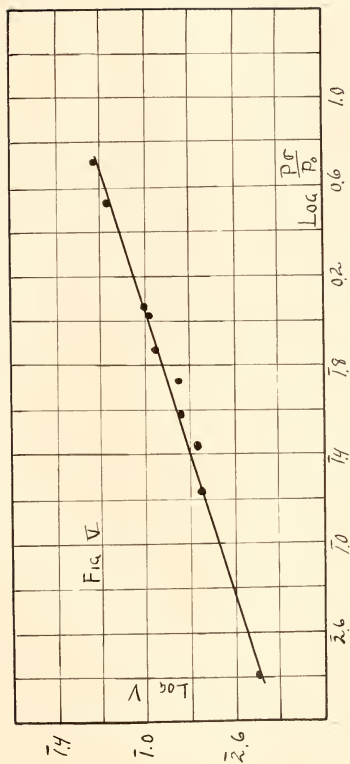
80











Biography

Levi Yorgey Davidhiser was born at New Hanover, Pennsylvania, April 6, 1885. He received his elementary education in the public schools of New Hanover and Bovertown, and Perkiomen School, from which institution he graduated in 1903. He taught in the public schools of his native County from 1905 - 1911. He then entered Ursinus College, from which institution he graduated in 1914 with the Degree of Bachelor of Arts. He again took up the teaching profession and continued in this work until he entered the Graduate School of Johns Hopkins University in 1917. He continued his work here for three years, pursuing the courses of Chemistry, Physical Chemistry and Mathematics.



















